INSTITUTO POLITÉCNICO DE TOMAR

ESCOLA SUPERIOR DE TECNOLOGIA

Unidade Departamental de Engenharias

Licenciatura em Engenharia Química e Bioquímica

INORGANIC CHEMISTRY (1st Year/2nd Semester)

EXERCISES SERIES

Academic Year 2017-2018

1st Exercises Series – Theories of Chemical Bonding

1. Consider the following pairs of atomic orbitals belonging to adjacent nuclei: a) 1s and 1s; b) 1s and $2p_x$; c) $2p_x$ and $2p_y$; d) $3p_y$ and $3p_y$; e) $2p_x$ and $2p_x$; f) 1s and 2s. Which ones can coalesce and form a sigma bond? Which can coalesce and form a pi bond? Which cannot coalesce (there is no bonding)? Admit that the x-axis is the internuclear axis, that is, the line joining the nuclei of the two atoms.

2. Use the hybridization of atomic orbitals to describe the bonds in the molecule AsH_3.

3. Determine the state of hybridization of the central atom of each of the following molecules: a) $HgCl_2$; b) AlI_3; c) PF_3. Describe the hybridization process and determine the geometry of the molecule in each case.

4. What are the hybrid orbitals of the carbon atoms in the following molecules?
   4.1. $CH_3 - CH_3$
   4.2. $CH_3 - CH = CH_2$
   4.3. $CH_3 - CH_2 - OH$
   4.4. $CH_3 - CH = O$
   4.5. $CH_3 - COOH$

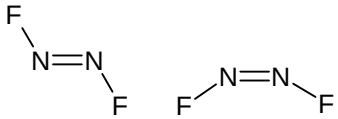
5. Justify that the chemical bond in O_2^{2-} is weaker than in O_2, but in O_2^+ is stronger (refer to the concept of molecular orbitals).

6. Put the following chemical species in order of stability: Li_2, Li_2^+ and Li_2^-. Use molecular orbital diagrams to justify the choice.

7. Write the electronic configuration of the B_2 molecule in the ground state. Is it a diamagnetic or paramagnetic molecule?

8. Indicate the number of σ and π bonds present in the HCN molecule.

9. The molecule with the formula N_2F_2 can exist in two alternative geometries:



   9.1. What is the hybridization of the N atom in the molecule?
   9.2. Which of the geometries has a non-zero dipole moment?

10. Of the following species, which has a longer bond length: F_2 or F_2^-?

11. Write the electronic configuration of the O_2 molecule in the ground state and show that it is a paramagnetic molecule.

12. Using the Theory of Valence Bond, describe the chemical bond in the molecules BeH_2 and H_2O. Justify.

13. Methanal, or formaldehyde, of formula CH_2O, has a flat structure with angles of approximately 120°. Using the valence bond theory, describe the different chemical bonds identifying, if necessary, the type of hybridization to which you resorted.

14. Predict which of the molecules should have dipole moment, draw the geometry of the molecules and the direction of the dipole moment in cases where it exists:
    BeF_2 BF_3 NH_3 PH_3 CH_4 H_2O H_2S

15. Considering only the atomic valence orbitals, how many molecular orbitals are formed by 100 Mg atoms? How many of these orbitals are occupied by electron pairs?

2nd Exercises Series – Electrochemistry

1. Complete and balance the following oxidation-reduction equations:
   1.1. $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$ (acid medium)
   1.2. $MnO_2 + PbO_2 \rightarrow Pb^{2+} + MnO_4^-$ (acid medium)
   1.3. $Cr_2O_7^{2-} + H_2SO_3 \rightarrow Cr^{3+} + HSO_4^-$ (acid medium)
   1.4. $CrO_4^{2-} + Fe(OH)_2 \rightarrow CrO_2^- + Fe(OH)_3$ (basic medium)
   1.5. $ClO^- + I^- \rightarrow Cl^- + I_2$ (basic medium)
   1.6. $Fe_3O_4 + MnO_4^- \rightarrow Fe_2O_3 + MnO_2$ (basic medium)

2. Some catalysts used in the production of gasoline are finely dispersed platinum on an inert solid support. Suppose the platinum dioxide, PtO_2, and the gaseous hydrogen react to form metal platinum and water.
   2.1. Indicate the oxidation number of platinum in both cases.
   2.2. What is the reducing agent?
   2.3. Calculate the mass of water produced together with 1 g of Pt.

3. Calculate the volume of a solution of $KMnO_4$ 0.05 M required to oxidize 2 g of $FeSO_4$ in an acidic solution.

4. Give the oxidation numbers of all elements in the following molecules and ions: a) Mg_3N_2; b) CsO_2; c) CO_3^{2-}; d) ZnO_2^{2-}; e) $NaBH_4$; f) WO_4^{2-}.

5. Combustion reactions are redox reactions. Is this statement false or true? Justify.

6. Knowing that the standard reduction potential of $MnO_4^-(aq)$ to $Mn^{2+}(aq)$ is 1.52 V and the standard reduction potential of $O_2(g)$ to $H_2O_2(g)$ is 0.68 V, justify the discoloration of the aqueous solutions of potassium permanganate by the addition of hydrogen peroxide (write the respective equation).

7. Calculate the reduction potential corresponding to the pair Cl_2/Cl^-, knowing that the standard reduction potential for H_2O_2/H_2O is 1.77 V and that the cell operating, under standard conditions, based on the reaction $H_2O_2(aq) + 2Cl^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + Cl_2(g)$ has an electromotive force equal to 0.41 V.

8. Calculate the reduction potential corresponding to the pair $Cr_2O_7^{2-}/Cr^{3+}$, knowing that the standard reduction potential for O_2/H_2O_2 is 0.68 V and that the standard cell operating on these redox pairs has an electromotive force equal to 0.65 V (write the equations of the half reactions and the redox reaction).

9. Check, based on electrode potentials, whether the reactions translated by the chemical equations can occur spontaneously (see table of potentials)

9.1. $I_2(s) + 2KBr(aq) \rightarrow 2I^-(aq) + 2K^+(aq) + Br_2(aq)$
9.2. $Cl_2(g) + 2KBr(aq) \rightarrow 2Cl^-(aq) + 2K^+(aq) + Br_2(aq)$

10. Predict whether the following reactions would occur spontaneously in aqueous solution at 25 °C. Consider the initial concentrations of dissolved species equal to 1 M.
    10.1. $Ca(s) + Cd^{2+}(aq) \rightarrow Ca^{2+}(aq) + Cd(s)$
    10.2. $2Br^-(aq) + Sn^{2+}(aq) \rightarrow Br_2(l) + Sn(s)$
    10.3. $2Ag(s) + Ni^{2+}(aq) \rightarrow 2Ag^+(aq) + Ni(s)$

11. Which of the following metals can react spontaneously with pure water? Write the reactions. a) Cu; b) Mg; c) Ag; d) Ca.

12. Suppose that in a given cell the reaction $N^{2+} + M \rightarrow N + M^{2+}$ occurs, where M denotes a metal and corresponds to a standard Gibbs energy variation of $\Delta G^0 = -69233\ J\ mol^{-1}$ at 25 °C. Calculate the standard potential value of this cell.

13. The potential of a cell consisting of a graphite electrode immersed in a solution of concentration $4x10^{-3}$ M in Fe^{3+} ions and $5x10^{-4}$ M in Fe^{2+} ions and a lead electrode immersed in a solution of concentration 0.022 M in Pb^{2+} ions at 25 °C is 1.0 V. The oxidation occurs in the lead electrode. Calculate the $E°(Pb^{2+}/Pb)$ knowing that $E°(Fe^{3+}/Fe^{2+})$ = 0.77 V.

14. Be the cell consisting of a manganese wire dipped in a 0.1 M manganese chloride solution ($MnCl_2$) and a silver plate dipped in a saturated solution of silver sulphide. $K_{ps}(Ag_2S) = 6.3x10^{-51}$.
    14.1. Schematically represent the cell.
    14.2. Calculate the electromotive force at 25 °C: $E°(Ag^+/Ag)$ = +0.80 V and $E°(Mn^{2+}/Mn)$ = -1.18 V.
    14.3. Calculate the equilibrium constant of the redox reaction present in the cell at 25 °C.

15. Calculate the standard cell potential constituted by the half-cell Zn/Zn^{2+} and by the SHE. What would be the electromotive force of the battery if $[Zn^{2+}]$ = 0.45 M, P_{H2}= 2 atm and $[H^+]$= 1.8 M?

16. Calculate the electromotive force of the following concentration cell:
    Mg(s) | Mg^{2+}(aq, 0.24 M) | KCl(sat) | Mg^{2+}(aq, 0.53 M) | Mg(s)

17. Calculate the mass of aluminum that is deposited in an electrolysis in a bath containing Al^{3+} ions having a current intensity of 40 A for 30 minutes.

18. A constant current is passed for 18 hours through an electrolytic cell containing $MgCl_2$. Calculate the current intensity knowing that $4.8x10^5$ g of Cl_2 was obtained.

19. What is the hourly production of chlorine gas from an electrolytic cell with the aqueous NaCl electrolyte and using a current of 1.5×10^3 A. The efficiency of the anode for the oxidation of Cl^- is 93%.

20. Chroming is applied by electrolysis to suspended objects in a dichromate solution according to the following (not corrected) half-reaction:

$$Cr_2O_7^{2-}(aq) + H^+(aq) + e^- \rightarrow Cr(s) + H_2O(l)$$

How much time (in hours) would it take to apply a chrome plating of 1×10^{-2} mm thickness to a bumper of an automobile with an area of 0.25 m^2, in an electrolytic cell using a current of 25 A?

21. The industrial purification of copper is done by electrolysis. Impure copper functions as an anode and the cathode is made of pure copper. The electrodes are immersed in a solution of $CuSO_4$. (A) Write the overall reaction of the process. (B) Assuming copper is contaminated with Zn and Ag, explain what happens to these impurities in electrolysis. (C) How many hours are required to obtain 1 kg of copper with a current of 18.9 A?

22. Before Hall and Héroult invented the electrolytic process, aluminum was produced by reducing its chloride with an active metal. What metals could you use to make aluminum by this method? (Hint: check the standard reduction potential table)

23. The same amount of electrical charge that deposits 0.583 g of silver crosses a solution containing a gold salt, having deposited 0.355 g on a certain electronic circuit. What is the oxidation state of gold in this salt?

24. It is intended to copper a steel sheet of a meter long and 30 cm wide in order to obtain a uniform layer of 0.02mm. If a current of 100 A is used, what is the time required for this process? Consider the copper density equal to 8.9 g cm^{-3}.

3rd Exercises Series – Introduction to Inorganic Chemistry

1. List three types of preliminary ore treatment. How do you designate useless materials?

2. Sometimes it is necessary to carry out a preliminary calcination of the mineral. Complete the following equation: PbS (s) + ... → ..... + ...

3. Select a metal from the electrochemical series that is suitable for reducing chromium (III) oxide at high temperature. Could this metal also be used in the reduction of manganese (II,III) oxide?

4. Which of the following compounds, iron chloride or sodium chloride, needs to be subjected to electrolysis to obtain the respective free metal? Justify.

5. Describe the reactions occurring in the process of obtaining iron on the blast furnace.

6. What is the Mond process? Indicate other types of metal purification.

7. How can you distinguish between solid conductors, semiconductors and insulators? How can a semiconductor become a conductor of electricity?

8. Why is potassium not usually prepared by electrolysis from one of its salts?

9. The second ionization energy of magnesium is only about twice that of the first ionization, while the energy of third ionization is about ten times greater. Justify this significant difference.

10. Why is aluminum not corroded like iron? How many hours will it take to deposit 664 g of Al in the Hall process with a current of 32.6 A?

11. Write the reactions of the three types of oxide with water. What kind of reactions are these? Describe the processes for obtaining hydrogen peroxide and sulfuric acid.

12. How can you prepare hydrogen fluoride? Is it safe to store this reagent in a glass container? Establish in descending order the acidic strength of the aqueous solutions of the hydrogen halides.

13. Describe the chlor-alkali process to obtain chlorine gas.

14. In its compounds, hydrogen has three types of bonding. Describe, using an example, each type of these bonds.

15. Sodium hydroxide is hygroscopic, that is, it absorbs moisture when exposed to the atmosphere. A student left a piece of NaOH on a watch glass and after a few days found that the piece was covered with a white solid. What is this solid?

16. Explain why:
    16.1. NH_3 is more basic than PH_3.
    16.2. NH_3 has a higher boiling point than PH_3.
    16.3. PCl_5 existes but NCl_5 does not.
    16.4. N_2 is more inert than P_4.

17. Describe two reactions in which sulfuric acid acts as an oxidizer.

18. Show that chlorine, bromine and iodine are not very different, describing their behavior:
    18.1. With hydrogen.
    18.2. In the production of silver salts.
    18.3. As oxidizing agents.
    18.4. With sodium hydroxide.
    18.5. In what aspects does fluorine not behave like a typical halogen?

19. Establish the electronic configuration of iron and manganese, and their most common ions.

20. List the formulas / names of the following complexes:
    20.1. Tetramine copper (II) sulphate
    20.2. Hexaaquachromium (III) bromide
    20.3. Tetracyanonickelate(II) ion
    20.4. $K_3[CoBr_6]$
    20.5. $NH_4[Ag(CN)_2]$
    20.6. AgF_4^-

21. Which species does not act as a ligand in the formation of complexes? Justify.
    21.1. CN^-
    21.2. H_2O
    21.3. CO
    21.4. NH_4^+
    21.5. Cl^-

22. What is the oxidation number of the central metal atom in the following compounds:
    22.1. $[Ru(NH_3)_5(H_2O)]Cl_2$
    22.2. $[Cr(NH_3)_6](NO_3)_3$

23. Draw the geometric isomers of the complex tetraaminodichlorocobalt (III) ion.

24. The blue hydrated cupric ion absorbs radiation at 600 nm. Calculate the energy variation involved in the electronic transition. Based on the crystalline field theory, how do you explain this phenomenon? Why the copper solution is stronger blue if we add ammonia? And what would be the effect if we added sodium chloride?

4th Exercises Series –Nuclear reactions and nuclear stability

1. A radio-221 atom emits an α particle. How many protons and neutrons are there in the nucleus of the resulting atom?

2. In what atom does $^{210}_{82}Pb$ transform itself by emitting a β particle?

3. What particles are emitted during each of the following nuclear disintegrations::
   3.1. $^{56}_{27}Co \rightarrow {}^{56}_{26}Fe + \cdots$
   3.2. $^{241}_{94}Pu + {}^{4}_{2}\propto \rightarrow {}^{243}_{95}Am + \cdots$
   3.3. $^{89}_{36}Kr \rightarrow {}^{88}_{36}Kr + \cdots$

4. An atom of a radioactive element $^{239}_{93}X$ undergoes disintegration, emitting an α particle and β particles. What is the number of β particles emitted and what is the number of neutrons of the resulting atom, knowing that it is a isotope of the element X?

5. Suppose that an element $^{238}_{92}A$ Emits a particle α, a particle β and a γ-ray. What is the element (atomic number and mass number) that forms after these emissions?

6. Uranium-235, when bombarded with a z-particle, reacts as follows: $z + {}^{235}_{92}U \rightarrow {}^{94}_{36}Kr + {}^{139}_{56}Ba + 3z$. Identify, justifying, what is the particle z.

7. The symbol $^{12}_{6}C$ (α, n) is used to denote a nuclear reaction in which an α particle collides with a C-12 nucleus to form another isotope and emits a neutron. Write the nuclear reaction for this process.

8. Calculate the nuclear cohesion energy (in J) and the cohesion energy per nucleon of $^{209}_{83}Bi$ (208.9804 u).

9. The series of the naturally occurring radioactive decay beginning with $^{238}_{92}U$ ends with the formation of the stable atom $^{206}_{82}Pb$. The decay is achieved through the emission of α and β particles. How many emissions of each type are involved in this series?

10. What is the half-life of a radioisotope if 16 g of it decays to 0.50 g in 2 hours?

11. A gram of Ra-226 was stored in a container in 1974. In what year 1/8 of the Ra-226 of the initial mass will be found in this container, knowing that the half-life of this radioisotope time is 1620 years?

12. The half-life of $^{210}_{84}Po$ is 140 days. With 100 g of this radioactive sample, what mass will remain after 420 days?

13. Carbon-14 is produced in the atmosphere through the interaction of neutrons from cosmic radiation with common nitrogen-14 atoms.
    13.1. Write the nuclear decay equation for carbon-14.
    13.2. Knowing that the half-life of C-14 is approximately 5730 years, and that a skeleton of an animal has a C-14 rate equal to 12.5% of normal, how many years ago has this animal died?

14. It takes 5 years for Co-60 to lose half of its radioactivity. What is the percentage of the original activity that will remain after 20 years?

15. If the half-life of $^{140}_{56}Ba$ is 12.75 days, how many atoms of $^{140}_{56}Ba$ will remain after nine weeks if there were initially 2.4 moles of atoms?

16. How long will it take for 3.8×10^{24} atoms of $^{100}_{47}Ag$ to disintegrate into 2.93×10^{23} atoms, if the half-life of $^{100}_{47}Ag$ is 24.6 seconds?

17. The disintegration rate of the carbon-14 of a sample obtained from a young tree is 0.260 disintegrations per second and per gram of sample. Another sample prepared from an object recovered from an archaeological excavation has a disintegration rate of 0.186 disintegrations per second per gram. How old is the object?

18. List the isotopes that can undergo nuclear fission.

19. Describe some of the applications of isotopes in Chemistry and Medicine.

20. Describe the operation of a Geiger counter.